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Several combustion behaviours of the whistling pyrotechnic based on potassium perchlorate and sodium benzoate

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Abstract

This study reported the influence of oxidizer-fuel content and particle size of the fuel on combustion characteristics of the whistling mixture based on potassium perchlorate and sodium benzoate such as heat of explosion, the specific volume of gaseous products, burning rate and intensity of whistling sound. From the analysis of theoretical prediction and experimental data, we selected an appropriate ingredient and particle sizes of components in order to archive the optimal intensity of the whistle. The whistling pyrotechnic has a relatively low sensitivity to friction and could be safely used for several military and civilian applications.

Keywords. Whistling pyrotechnics, potassium perchlorate, sodium benzoate, combustion.

1. INTRODUCTION

Whistling pyrotechnics are a particular type of pyrotechnic compositions when pressed into a tube and ignited burn with a whistling sound. These pyrotechnic compositions have been known and used in military and civilian applications for many years.[1-8] Based on ingredients whistling compositions were divided into several mixtures such as gallic acid and potassium chlorate, potassium picrate and potassium nitrate, potassium benzoate and potassium perchlorate, etc.[1] Maxwell W.R. is the first scientist who has detail studied on fundamental combustion behaviors of a whistling pyrotechnic based on potassium perchlorate and potassium benzoate.[2] In the own article, Maxwell has shown the variation of the frequency of whistling sound, the burning rate with compositions, the effect of the frequency on the burning rate, the quality of the whistle from tubes in different diameters, etc. He also explained the formation of the whistling effect by burning intermittently from layer to layer in the pressed composition. Mixtures containing gallic acid and potassium picrate have a very high sensitivity to mechanical actions such as shock and friction. So in recent years, they are not widely used in reality.[3,4]

Selkuk Oztap concentrated on a composition containing potassium chlorate, sodium salicylate, lubricant and ferric oxide.[5] He used paraffin oil, castor oil or vaseline as the lubricant and ferric oxide as a catalyst to decompose potassium chlorate. Here the lubricant decreases the sensitivity of potassium chlorate, regards moisture absorption by sodium salicylate and inhibits flying dust from the composition during the manufacturing process. However, potassium chlorate has been involved in a large percentage of serious accidents at fireworks manufacturing plants, and it must be treated with great care if it is used at all. In the USA, factories have greatly reduced their use of potassium chlorate as well, replacing it with the less-sensitive potassium perchlorate in many formulas.[7]

In order to successfully prepare an effective and safely whistling pyrotechnic used for military and civilian purposes, we have studied on the influence of oxidizer-fuel content and particle size of the fuel on several burning characteristics. The composition contains potassium perchlorate as an oxidizer, sodium benzoate as a fuel, liquid paraffin as a lubricant and ferric(III) oxide as a catalyst of thermal decomposition of the oxidizer.

2. MATERIALS AND METHODS

2.1. Materials

Powder potassium perchlorate ($KClO_4$) which has particle sizes in a range of 50÷88 μm, powder sodium benzoate (C_6H_5COONa) which has three types of particle size in ranges of 88÷402 μm, 60÷88 μm and

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50÷60 μm, fine powder ferric(III) oxide (Fe_2O_3), liquid paraffin, toluene were obtained from Chinese Company Xilong. All chemicals used were of p-grade.

2.2. Preparation of whistling pyrotechnic samples

The samples of pyrotechnic compositions were prepared as follow. The required quantities of different ingredients of dry $KClO_4$ and C_6H_5COONa powders were weighed and mixed by brushing them from 5 to 6 times through 15 #/cm sieves. Liquid paraffin was dissolved in toluene in order to receive a 10 wt.% solution. After that, the solution was kneaded with ferric oxide and a mixture of potassium perchlorate and sodium benzoate. Amount of the solution and ferric oxide were used in such a way that the contents of liquid paraffin and ferric oxide in the pyrotechnic samples are 3.8 % and 1.5 % by weight (over 100 %), respectively. The wet pyrotechnic mixtures were preliminarily dried in the air and then passed through the 38 #/cm sieves. Finally, the whistling pyrotechnic samples were dried at a ceertain temperature in the range of 50÷60 ºC for 2 hours.

2.3. Characterization

The heat of the explosion was determined by using a Parr-6200 calorimeter with 2 grams of sample weight. Thereafter, the pressure in the calorimeter bomb was measured on a Lutron-9017 manometer and the volume of gaseous products was calculated as follow:

$$V = \frac{273}{T_c} \cdot \frac{\Delta P \cdot V_b}{1000 \cdot m} \quad (1)$$

where, V - the volume of gaseous products, ml/gr; ΔP - the difference between values of pressure in the combustion chamber before and after measurement, mbar; T_c - the temperature of the combustion chamber, which equals the room ambient temperature, K; V_b - the volume of the combustion bomb equals to 334 ml.

The burning rate was obtained as a ratio between the traveling distance of the combustion front and the corresponding time interval determined by using a digital camera. To measure the burning rate, the whistling pyrotechnic was pressed into a steel tube with 4.2 mm in diameter to 1.9 gr/cm^3 of density. The distance between the starting and ending points on the steel tube is 19.3 mm. The autoignition temperature was determined by a AET-700 Automatic Explosion Temperature Tester according to STANAG 4491. The steel tube with 8.6 mm in diameter and 50 mm of length used to measure the intensity of sound was loaded by the pyrotechnic composition to 1.9 gr/cm^3 of density. The intensity of the whistle was recorded on a Sound Level Meter Model GM1356 with the distance between end close of the tube and apparatus was 60 cm. The friction sensitivity was carried out by a BAM Friction Tester according to STANAG 4487.

3. RESULTS AND DISCUSSION

3.1. Effect of oxidizer-fuel content on combustion characteristics

In order to assess the influence of oxidizer/fuel content on combustion characteristics of the whistling composition, we prepared samples having $KClO_4/C_6H_5COONa$ ratios as follow: 60.3/34.4; 63.3/31.4; 66.3/28.4; 69.3/25.4; 72.3/22.4; 76.3/18.4; 80.3/14.4; 84.3/10.4. Contents of Fe_2O_3 and liquid paraffin are 1.5 and 3.8 wt.% respectively. Particle sizes of $KClO_4$ and C_6H_5COONa were 60÷88 μm. The theoretical and experimental values of the essential combustion characteristics of the whistling mixture samples are shown in Table 1. The parameters Q_v, V_0, and T_c were predicted by using the computer program named "COMBUS 1.0".[9]

The heat of explosion and volume of gaseous products. Figure 1 shows the influence of oxidizer content on the heat of the explosion and the volume of gaseous products of the mixture. It is clear that heat of explosion increased approximately linearly with the increase in mass content of $KClO_4$ in a range from 60.3 to 80.3 % and will approximately linearly decrease if continuously increase the mass content of $KClO_4$ in a range from 80.3 to 84.3 %. The highest value of the heat of explosion (1185 cal/gr) was observed at 80.3 wt.% potassium perchlorate (the M7 sample). The oxygen balance of the sample is about zero. Thus, the whistling mixture corresponds to the ideal stoichiometry. The variation of the volume of gaseous products was inconsistent with the change of heat of the explosion. The M7 sample had the lowest value of the volume of gaseous products (about 203 ml/gr). Besides, predicted values of Q_v, and V_0 by the "COMBUS 1.0" computer program for the pyrotechnic samples were in reasonable agreement with the measured data. With the samples having oxygen balance values are considerably smaller than zero, the deviation between predicted and experimental data is quite considerable because the calculation omitted generation of solid carbon in combustion products, which was confirmed by black color of solid combustion products of M1÷M5 samples in the calorimeter bomb. Combustion products of the M6÷M8 ($K_b \sim 0$) were pink of Fe_2O_3,

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it indicates that solid carbon was not generated. However, the heat of the explosion is not the most important parameter to select an ingredient for the whistling mixture.

Table 1: The influence of oxidizer/fuel ratios on combustion characteristics of whistling compositions

Samples	Ingredients (wt.%)		K_b	Q_v	V_0	u	I	T_b
	$KClO_4$	C_6H_5COONa	(%)	(kcal/kgr)	(l/kgr)	(mm/s)	(dB)	(°C)
M1	60.3	34.4	-42.7	576	488	3.6	116	465
M2	63.3	31.4	-36.3	668	454	4.4	119	477
M3	66.3	28.4	-29.9	749	407	5.1	124	471
M4	69.3	25.4	-23.5	837	359	5.3	123	450
M5	72.3	22.4	-17.1	927	312	5.7	122	461
M6	76.3	18.4	-8.6	1068	251	5.6	119	474
M7	80.3	14.4	-0.1	1185	203	5.2	99	466
M8	84.3	10.4	8.4	969	220	3.8	82	463

*Note: K_b - oxygen balance, Q_v - heat of explosion, V_0 - volume of gaseous products, T_c - adiabatic combustion temperature, T_b - autoignition temperature, u - burning rate, I - intensity of whistles.

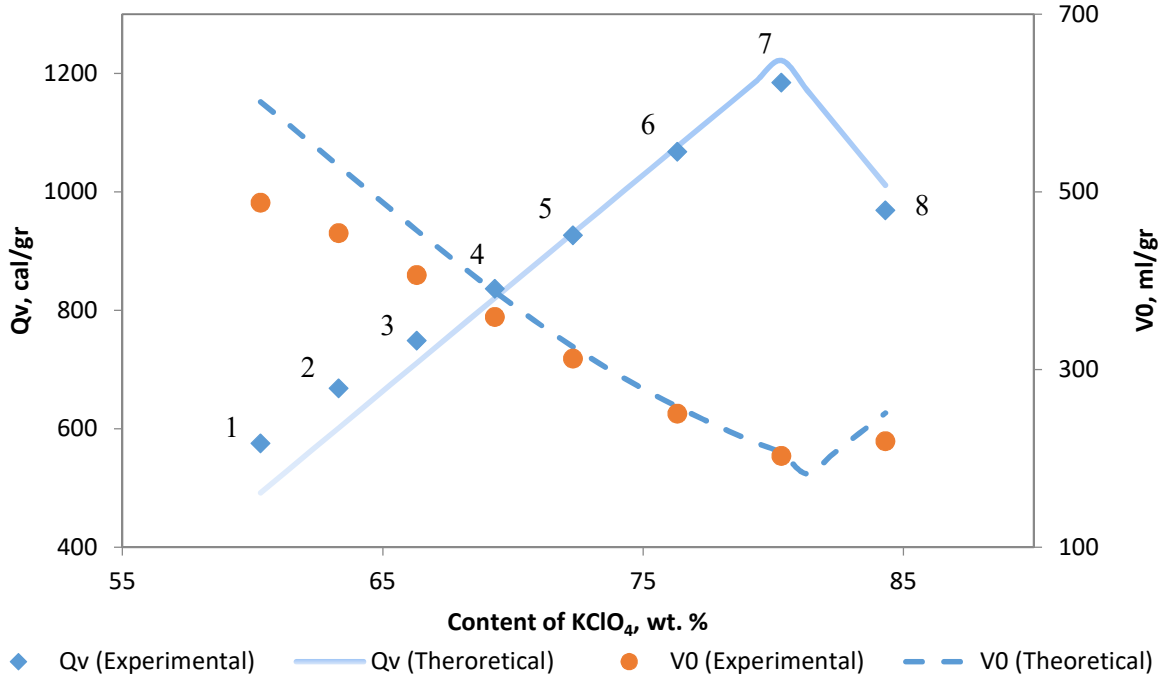

Figure 1: Variation of the heat of explosion and specific volume of gaseous products

The burning rate. As shown in figure 2, it is clearly that the burning rate increases with the rise of oxidizer content and reaches the maximum value at 72.3 wt.% of $KClO_4$ (the M5 sample), then will decreases if oxidizer content is continuously increased. Based on experimental data we found a regression equation of burning rate by oxidizer content. Using the equation could regulate the value of burning rate satisfying practice demand.

The intensity of whistling sound. The intensity of whistle is the most important factor of the whistling composition because it decides the ability to use the mixture. Therefore, we selected ingredient in order to maximize the intensity of whistling sound. As indicated in figure 3, the intensity of whistling sound increased from M1 to M3 samples, then slowly decreased to M6 sample and rapidly decreased with M7, M8 samples. The variation of the level of the whistle was interpreted by combining the influence of heat of explosion, the volume of gaseous products, and burning rate. The M3 sample has the highest value of the level of whistle and deviation between M3÷M5 samples was slight. Because the price of sodium benzoate is lower than potassium perchlorate,

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the ingredient of M3 sample was chosen to carry on the next studies.

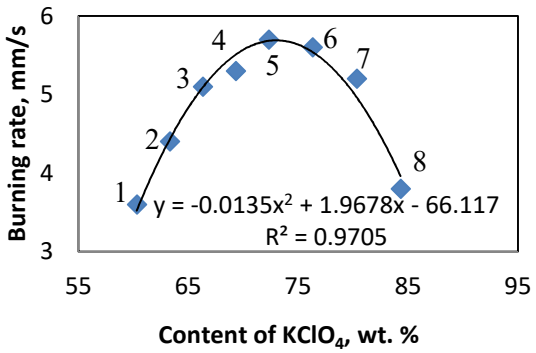

Figure 2: Variation of burning rate by oxidizer content

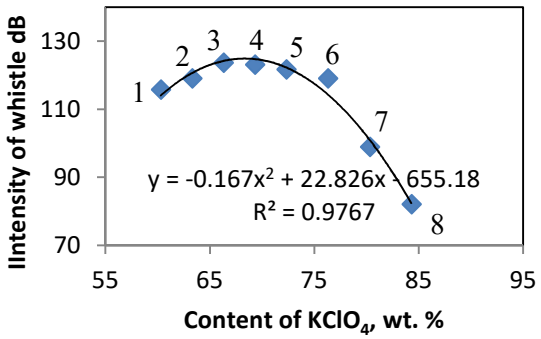

Figure 3: Variation of the intensity of whistling by oxidizer content

The autoignition temperature. The value of the Spearman correlation coefficient r between oxidizer content and the autoignition temperature of M1÷M8 samples was -0.13. Because of $|r| < 0.3$, no correlation between ingredients and autoignition temperatures was found to be existed.

3.2. Effect of particle size of sodium benzoate on combustion characteristics

We prepared whistling composition samples with the M3 ingredient and particle size of potassium perchlorate in a range of 50÷88 µm but three different types of particle size of sodium benzoate, concretely as follows in ranges of 50÷60 µm, 60÷88 µm, and 88÷402 µm. With these samples, we only measured values of burning rate and intensity of whistle. Received results were displayed in Fig. 4.

From Fig. 4, it is clear that the particle size of sodium benzoate is smaller, burning rate of the respective sample is bigger. This phenomenon could be explained by the rise of decomposition time of sodium benzoate particle having bigger sizes.

However, the deviation of burning rates between samples containing sodium benzoate in ranges of 50÷60 µm and 60÷88 µm was negligible. Similarly, the pyrotechnic composition containing sodium benzoate with smaller particle size has a lower intensity of whistling sound. In addition, the variation of particle size from in a range of 50÷60 µm to 60÷88 µm does not negligibly change the intensity of whistling sound. It indicates that the sodium benzoate with the particle size in a range 50÷88 µm can be used for economic reason.

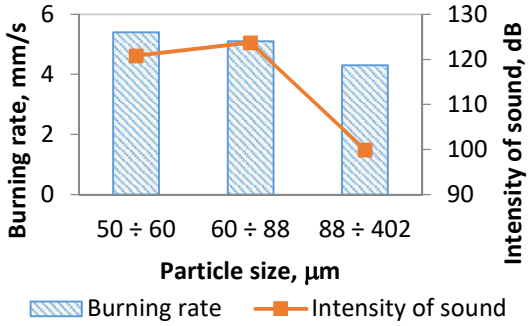

Figure 4: Influence of the particle size of sodium benzoate on burning rate and intensity of whistle

3.3. Other combustion behaviors of the selected ingredient of whistling mixture

The decay of the frequency of whistling sound with burning time was shown in Fig. 5. This phenomenon may be interpreted as follows. By the burning time, tube length above the composition was increased. This causes the time need to pressure wave propagates from the combustion front to the end of the tube also is gone up. As is well known whistling sound is formed by repeat propagation of pressure wave in the tube and frequency of whistling sound is inversely proportional with the propagation time of pressure wave.

The friction sensitivity. The recorded value of friction sensitivity of the whistling pyrotechnic was 32.4 kg according to STANAG 4487 (one explosion among six tests). In the meantime friction sensitivity of other explosives such as: RDX - one explosion among ten tests at 12.4 kg of weight; HMX - one explosion among 10 tests at 11.6 kg of weight; PETN - one explosion among 10 tests at 6.4 kg of weight; LX-11-0 - one explosion among 10 tests at 32.4 kg of weight. Thus the whistling pyrotechnic is relative safety to friction action in manufacturing, storage, and transport.

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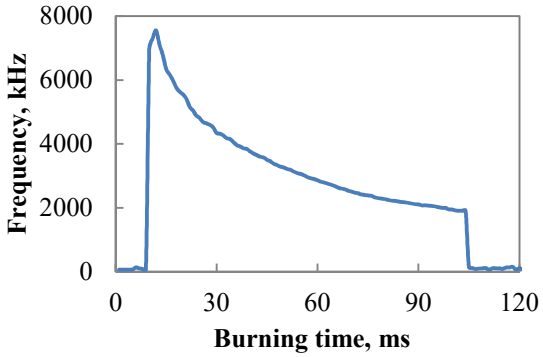

Figure 5: Variation of the frequency of whistling sound with burning time

The experiment of the ability to use the whistling mixture in reality. The pyrotechnic mixture was pressed to form a cylinder with 15.1 grams of weight, 24.5 mm in diameter and 16.67 mm of length. After that combining 3 cylinders to form a block, then charging into the model of signal mines being an aluminum tube having 25 mm in diameter and 10 cm of length. The experiment shows that burning time was 9.6 seconds and the whistle could be well heard from 500 meters of distance. Thus the whistling composition could be used in military and civilian applications.

4. CONCLUSION

The whistling pyrotechnic based on potassium perchlorate and sodium benzoate was successfully prepared. The optimal ingredient and particle size of raw materials were determined by the intensity of whistles. The pyrotechnic contains 66.3 wt.% of potassium perchlorate, 28.4 wt.% of sodium benzoate, 3.8 wt.% liquid paraffin and 1.5 wt.% ferric oxide. All potassium perchlorate and sodium benzoate have the particle size in a range of 50÷88 μm. The pyrotechnic composition has the heat of explosion of 749 cal/grams, burning rate of 5.1 mm/s at 1.90 gr/cm^3 of density and the highest intensity of whistles. Experiments also indicated that the pyrotechnic has similar combustion behaviors with others and could be safely used for military and civilian purposes as well.

REFERENCES

1. Takeo Shimizu. Fireworks: The Art of Science and Technique, Pyrotechnica Publication, Texas, **1981**.
2. W. R. Maxwell. Pyrotechnic Whistles. Symposium (International) on Combustion, **1953**, *4(1)*, 906-914.
3. A. A. Shidlovsky. Fundamentals of pyrotechnic, *Mashinostroenhie*, Moscow, **1964**.
4. K. L. Kosanke, B J. Kosanke, Clive Jennings White. Pyrotechnic Reference Series: No.2, Lecture Notes for Pyrotechnic Chemistry, *Journal of Pyrotechnic Inc*, **2004**.
5. Selcuz Oztap. The Pyrotechnic whistle and its applications, *Pyrotechnica XI*, **1987**, 49-54.
6. H. Ellern. Military and civilian pyrotechnics, *Chemical Publishing Company Inc*, **1968**.
7. J. A. Conkling. Chemistry of Pyrotechnics: Basic Principles and Theory, *Marcel Dekker Inc*, **1985**.
8. V. E. Melnhikov. Modern Pyrotechnic, Moscow, **2014**.
9. Dam Quang Sang, Nguyen Van Tuan. The prediction of composition of combustion products and energetic-ballistic characteristic of gun propellants, *Journal of Science and Technology*, **2017**, *82*, 156-163.
10. S. L. Richard, F. M. Frances. LLNL Small-scale friction sensitivity (BAM) test, Lawrence Livermore National Laboratory, **1996**.

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